



Chemomechanics of acidic ionomers: Hydration isotherms and physical model

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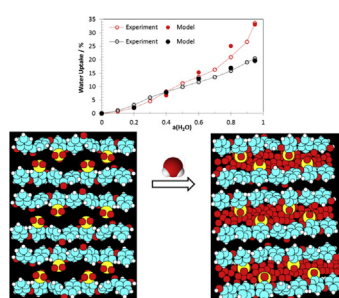
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HIGHLIGHTS

- Hydration isotherms of acidic ionomers described by physical model without any fitting parameter.
- Only two constants related to ionomer properties: deformation and free volume parameters.
- Significance of experimental strategies for improvement of hydration and durability discussed.
- Cross-linking of ionomers reduces swelling at high humidity, but also dehydration at low humidity.

GRAPHICAL ABSTRACT



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ABSTRACT

The hydration isotherms of various ionomers (Nafion, Sulfonated Poly-Ether-Ether-Ketone, Sulfonated Poly-Phenyl-Sulfone) were measured and described by a thermodynamic model, assuming ideality and a linear relation between the thermodynamic osmotic pressure and the volume of the internal electrolytic solution. The only two parameters used are related to measurable physical properties: the deformation parameter, inversely proportional to the elastic modulus of the ionomer, and the free volume parameter. The experimental trends are well reproduced by the model, showing that it captures the main physical features and is suitable for semi-quantitative analysis of ionomer hydration. It indicates that the ionomers behave in good approximation like elastic solids in the studied range of water activities ($0 < a(\text{H}_2\text{O}) < 0.95$). The implications for practical improvement of ionomer properties by thermal cross-linking and annealing treatments are discussed. Cross-linked ionomers do not only better resist swelling at high humidity, but also dehydration at low humidity, which should increase their durability.

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1. Introduction

Ion conducting polymers (also called ionomers [1–7]) are a fascinating field of research with many high added value applications, including energy and environment. For example, ionomers can be applied for waste water treatment [8], in proton and anion exchange membrane fuel cells (PEMFC [9–14] and AEMFC

[15,16]), and as separation membranes in redox flow batteries [17,18].

Hydrated ionomers present a subtle nanocomposite structure: ionic conduction takes place in hydrated nanometric channels, percolating through the ionomer matrix, which is made of the highly stable macromolecular backbones and is responsible for the thermal, chemical and mechanical properties of the ionomer [4,19–22]. This particular nanostructure allows decoupling ionic motion from the other properties.

Although water is necessary to allow ionic conduction, it weakens on the same time the mechanical stability of the matrix,

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by reducing the interactions between macromolecular chains, and acts as plasticizer. In fact, dehydration at low humidity or temperatures above 80 °C leads to loss of proton conductivity [21,23], but, on the other hand, the effect commonly known as “swelling” occurs at high humidity, when large quantities of water enter the polymer membrane due to the osmotic pressure [24–27]. This large water uptake is accompanied by an important deterioration of the mechanical properties.

Swelling of ionomers reduces the durability of electrochemical devices, because the contact between the ionomer membrane and the electrodes, where the electrochemical reaction takes place, can get lost in the membrane-electrode assembly. In fuel cells, the large volume expansion or contraction observed on changes of water activity in the surrounding atmosphere leads ultimately to a device failure. Although ionomer swelling and its relation to the osmotic pressure of water are known for quite long time [28–31], they are not yet fully understood. Swelling of ionomer membranes forms part of the new research field of “chemomechanics”, which studies the interdependence of compositional changes and mechanical properties in solid materials. Understanding these phenomena requires a general conceptual framework to organize, generalize and extrapolate the experimental observations.

The equilibrium state of the hydrated ionomer is given by the minimum of the Gibbs free energy. The variation of Gibbs free energy during water uptake includes several contributions:

$$\Delta G = \Delta G_{\text{osmotic}} + \Delta G_{\text{elastic}} + \Delta G_{\text{interface}} + \Delta G_{\text{electro}} \quad (1)$$

The Gibbs free energy variation due to the osmotic pressure $\Delta G_{\text{osmotic}}$ is the driving force for the water uptake, which is opposed by the elastic deformation energy $\Delta G_{\text{elastic}}$ of the ionomer matrix. The interfacial energy term $\Delta G_{\text{interface}}$ includes the contribution of the hydrated domain-matrix interfaces with the Laplace pressure due to the interface curvature of hydrated domains in the ionomer that can be also included in the elastic term [32,33]. Finally, the electrostatic energy $\Delta G_{\text{electro}}$ takes into account the modification of Coulombic forces between ions during changes of the hydrated channel width [29]. The two last contributions are difficult to assess. The interface term depends on the morphology of the hydrated domains, which are generally considered spherical or cylindrical, but the exact morphology is still a matter of discussion [34,35]. The electrostatic term cannot be expressed by analytical equations and is only accessible numerically [29]. It is therefore difficult to use the complete Gibbs free energy variation for prediction of hydration properties of ionomers. A model for the description of the thermodynamics of water sorption in Nafion was presented some time ago by Datta et al. [36]; although it is rather complete, its practical application seems to be difficult due to the availability of ionomer parameters.

In this work, we will introduce a simplified physical model without any fitting parameter taking into account only the osmotic pressure and the elastic deformation terms. The two parameters used in the model are related to measurable properties of the studied ionomers: the elastic modulus and the free volume. If successful, this approach has the major advantage that predictions for the hydration properties of ionomers can be made.

The general features of the model will first be outlined and the used parameters will be introduced. The model will then be tested on literature data for Nafion and Sulfonated Poly-Ether-Ether-Ketone (SPEEK) and new hydration isotherms of SPEEK and Sulfonated Poly-Phenyl-Sulfone (SPPSU) with various degrees of cross-linking. Finally, the assumptions of the model will be critically assessed and predictions of the model for ionomer improvement will be discussed.

2. Physical model

In the following, the ionomer is considered as an elastic solid, mainly characterized from a mechanical standpoint by its elastic modulus. Furthermore, we make the following assumptions: 1) The system is ideal from a thermodynamic point of view. All activity coefficients are unity and the partial volumes are equal to the molar volumes (a very small negative volume of mixing, $\Delta V_{\text{mix}}/\lambda < -10^{-4} \text{ L mol}^{-1}$, was recently reported for SPEEK [22]). 2) The volume of the anions fixed on the macromolecular backbone is considered a part of the ionomer matrix. 3) Protons are completely dissociated (this assumption is reasonable for strong acidic ionomers, such as Nafion or Sulfonated Aromatic Polymers).

2.1. Thermodynamic osmotic pressure

During a hydration experiment, the electrolytic solution inside the elastic ionomer matrix is in contact with a constant water vapor activity. Under these conditions, water passes into the electrolytic solution (at higher water activity) or leaves it (at lower water activity), until the chemical potential of water inside and outside the ionomer is identical. The pressure difference at equilibrium is called the thermodynamic osmotic pressure π , which can be calculated from the expression [37]:

$$\pi = \frac{RT}{V_0} \ln \left(\frac{a(\text{H}_2\text{O})}{x_{0,\text{el}}} \right) \quad (2)$$

In this equation, R is the gas constant, T the absolute temperature and $a(\text{H}_2\text{O})$ is the water activity in the vapor phase. $x_{0,\text{el}}$ is the molar fraction of water in the electrolytic solution inside the hydrated ionomer, $(1 - x_{0,\text{el}})$ being the molar fraction of protons. V_0 is the partial molar volume of water, which can be assumed to be independent of pressure in condensed phases; it is considered equal to the molar volume (0.018 L mol^{-1}).

2.2. Determination of the equilibrium hydration number and water uptake

The volume of the inner electrolytic solution V_{el} is equal to the total measured volume V_{wet} of the wet ionomer minus the volume of the incompressible hydrocarbon matrix, including the anionic groups fixed to the channel walls, V_{matrix} :

$$V_{\text{wet}} = V_{\text{matrix}} + V_{\text{el}} \quad (3)$$

The volume of the inner electrolytic solution V_{el} can be also written:

$$V_{\text{el}} = \sum_i n_i V_i = n_0 V_0 + n_1 V_1 \quad (4)$$

In this equation, n_0 and n_1 are the mole numbers of water molecules and of compensating protons and V_0 and V_1 are their molar volumes ($V_1 \approx 0$). n_1 can be calculated from the ionic exchange capacity (IEC in mol kg^{-1}) and the dry density of the ionomer. One can at this point also include other components in the model, for example solvent remaining from the casting process, by adding other terms in the sum of Equation (4).

A linear relationship is now postulated between V_{el} and the thermodynamic osmotic pressure π :

$$V_{\text{el}} = a\pi + b \quad (5)$$

This expression describes in a general way the elastic properties of a polymer at moderate pressures [28]. The values of a and b depend upon the specific ionomer considered. A change of the mole

number of water n_0 changes V_{el} in Equation (4), but also in Equation (5) by a modification of the osmotic pressure π .

The equilibrium mole number of water molecules, $n_{0,eq}$, can now be calculated by the simultaneous solution of Equations (2), (4) and (5); this can be done numerically or by graphical means. According to the definitions of molar quantities exclusively used in this work, $n_{0,eq}$ is directly equal to the hydration number or water uptake coefficient λ , conventionally defined as:

$$n_{0,eq} = \lambda = \frac{n(\text{H}_2\text{O})}{n(\text{SO}_3\text{H})} = \frac{\text{WU}}{100 \times \text{IEC} \times M(\text{H}_2\text{O})} \quad (6)$$

The calculation of the water uptake WU (in %) is then straightforward knowing the IEC of the ionomer ($M(\text{H}_2\text{O}) = 0.018 \text{ kg mol}^{-1}$). WU is defined by the ionomer mass in dry (m_{dry}) and wet (m_{wet}) conditions:

$$\text{WU} = 100 \times \left(\frac{m_{wet} - m_{dry}}{m_{dry}} \right) \quad (7)$$

2.3. Physical meaning of the phenomenological parameters a and b

An important point is the physical meaning of the two parameters a and b in Equation (5). The experimentally measured volume of the ionomer in the dry state, V_{dry} , is the sum of the volume of the incompressible macromolecular chains, V_{matrix} , including the fixed acidic groups, and the free volume, V_{free} , accessible between polymer chains:

$$V_{dry} = V_{matrix} + V_{free} \quad (8)$$

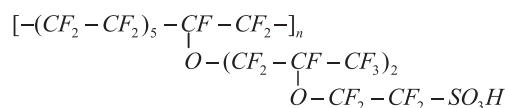
V_{dry} (in L mol^{-1}) can be calculated using the molar mass of the ionomer repeat unit divided by its dry density.

In membrane science, the free volume is often estimated from the Bondi equation [38–40]:

$$V_{free} = V_{dry} - 1.3 \cdot V_{vdw} \quad (9)$$

V_{vdw} is the Van der Waals volume that can be assessed from group contributions [38] or atomic contributions [41] reported in the literature. The fractional free volume values of polymers lie typically in a range 10–25% [39].

Let us give an example of calculation of the free volume for the case of Nafion. The formula of Nafion is written as:



The group contributions reported by Bondi [38] (using for the sulfonic acid group an increment of 0.029 L mol^{-1}) give a Van der Waals volume of 0.326 L mol^{-1} ; the atomic contributions reported by Zhao et al. [41] add to 0.316 L mol^{-1} in good agreement with the previous value. The density of dry Nafion 117 is $(2.0 \pm 0.2) \text{ kg L}^{-1}$, in agreement with Ref. [52]; the IEC being $0.909 \text{ mol kg}^{-1}$, this gives a dry volume $V_{dry} = 0.55 \text{ L mol}^{-1}$. Applying Equation (9), we obtain a free volume of 0.133 L mol^{-1} , about 25% of the dry volume.

Considering the Equations (3) and (5) and (8), we can write the identity:

$$V_{wet} - V_{dry} = a\pi + b - V_{free} \quad (10)$$

The thermodynamic osmotic pressure π of the water is opposed by the deformation pressure P of the ionomer, due to the stretching of the matrix. In equilibrium, the absolute values of π and P are

identical. For an elastic ionomer, following the treatment by Flory [42] and Gregor [29], the deformation pressure P and the volume strain of the ionomer, due to the elastic stretching of the network, are related by the elastic modulus E of the ionomer:

$$P = \frac{V_{wet} - V_{dry}}{V_{dry}} E \quad (11)$$

Assuming isotropic deformation, this equation is analogous to the Hooke law for one-dimensional deformation of an elastic solid. Comparing Equations (10) and (11), we can finally identify in Equation (5):

$$a = \frac{V_{dry}}{E} \text{ and } b = V_{free} \quad (12)$$

We will in the following call a “deformation parameter” and b “free volume parameter”.

2.4. Properties of the physical model and examples of calculations

Fig. 1 shows the evolution of the osmotic pressure π and the resulting water uptake WU as function of the molar fraction of water inside an ionomer for an outside water activity of 1. The parameters used for the calculation are: $\text{IEC} = 0.9 \text{ mol kg}^{-1}$, $a = 1.5 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$ and $b = 0.15 \text{ L mol}^{-1}$.

The thermodynamic osmotic pressure is very high when the water content in the ionomer is very low and $x(\text{H}_2\text{O})$ tends towards zero (the slope is infinity at $x(\text{H}_2\text{O}) = 0$, see Equation (2)). On the other side, the water uptake (and swelling) becomes very large when $x(\text{H}_2\text{O})$ tends towards 1. One can ensure that thermodynamics are respected by checking that:

$$\left(\frac{d\pi}{dx_{\text{H}_2\text{O}}} \right)_{x_{\text{H}_2\text{O}} \rightarrow 1} = \frac{RT}{V_0} \approx 1376 \text{ bar} \quad (13)$$

Fig. 2 shows an example of a graphical resolution: Equations (4) and (5) are simultaneously solved at the intersection of the two

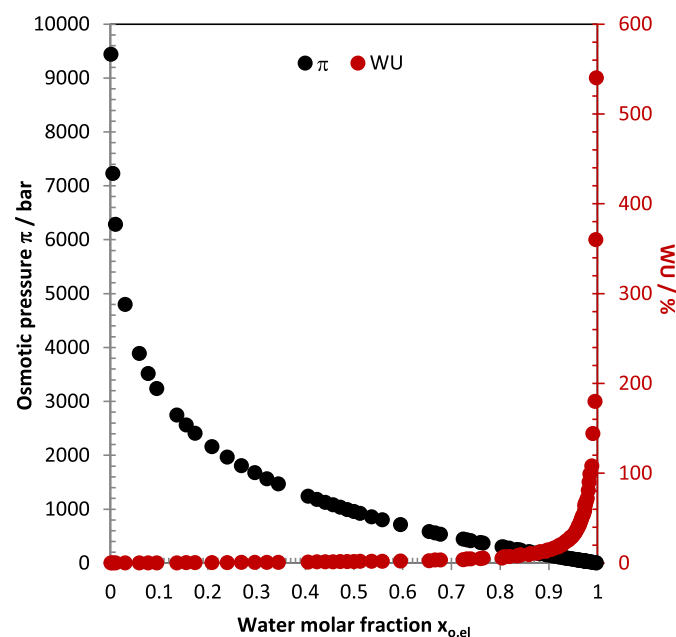


Fig. 1. Osmotic pressure and water uptake as function of the molar fraction of water inside an ionomer. The outside water activity is taken as 1. The parameters used for the calculation are: $\text{IEC} = 0.9 \text{ mol kg}^{-1}$, $a = 1.5 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$ and $b = 0.15 \text{ L mol}^{-1}$.

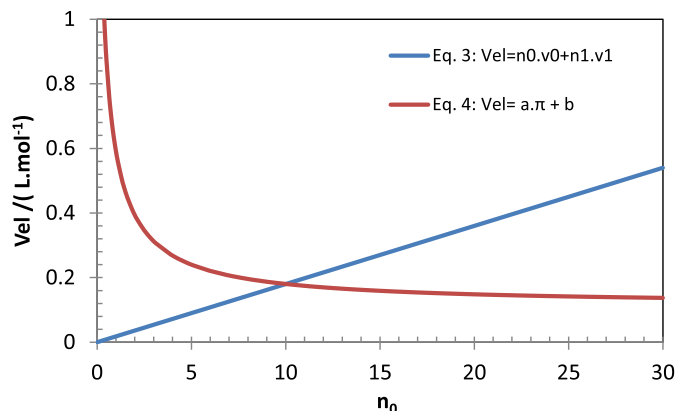


Fig. 2. Graphical determination of the equilibrium hydration number $n_{0,eq}$; in this case, $n_{0,eq} = 10$. The parameters used for the calculation are: $a(\text{H}_2\text{O}) = 0.95$, $\text{IEC} = 0.9 \text{ mol kg}^{-1}$, $a = 5 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$ and $b = 0.15 \text{ L mol}^{-1}$.

curves, where the equilibrium value of $n_{0,eq} = \lambda$ can be read (in this case $n_{0,eq} = 10$). This example is shown only for illustration; in practice, the faster numerical resolution is preferred. At the intersection, Equations (4), (5) and (12) give an expression for the water uptake coefficient:

$$\lambda \approx \frac{V_{\text{dry}}}{E \cdot V_0} \pi + \frac{V_{\text{free}}}{V_0} \quad (14)$$

3. Experimental

Poly-Ether-Ether-Ketone and Poly-Phenyl-Sulfone were obtained from various providers. The polymers were sulfonated by reaction with sulfuric acid at 50 °C. The ionic exchange capacity was varied by changing the reaction time; it was measured by acid-base titration, by NMR spectroscopy and by thermogravimetric analysis with comparable results. The experimental procedures can be found in previous publications [43–45].

The ionomer membranes were cast using either dimethylacetamide (DMAc) or dimethylsulfoxide (DMSO) as solvents. Typically, 25 mg of ionomer was dissolved in 250 mL solvent and cast on a Petri dish or using a home-made doctor-blade type apparatus. The solvent was then evaporated by thermal treatment at various temperatures. Some membranes cast using DMSO were also subjected to higher temperature treatments in order to cross-link them *in situ*, as shown in previous publications [43,44,46–48].

The water uptake was measured by two different techniques.

1. **Isopiestic measurements.** Isopiestic sorption of water at 25 °C was determined by suspending an ionomer sample in a closed vessel above saturated aqueous solutions of LiCl, MgCl₂, NaBr and KBr (all chemicals from Sigma–Aldrich) to reach equilibrium with constant water activity: 0.15, 0.41, 0.58, and 0.79, respectively [49]. The samples were allowed to equilibrate for 240 h before removal from the vessel. The membranes were then weighed (m_{wet}), dried completely over P₂O₅, and weighed again (m_{dry}) to determine the water uptake at a given water activity.
2. **Thermogravimetric measurements.** The water sorption isotherms were recorded using a water sorption analyzer (TA instruments Q5000). Prior to all experiments, the membranes were dried *in situ* for 3 h at 80 °C under 0% RH. The samples were then equilibrated with water vapor at 25 °C under 0–95% relative humidity (RH). RH was modified in 5, 10 or 20% steps and the water uptake recorded at each step for 2 h. The water desorption isotherms were studied by successively decreasing

the water activity. The hysteresis between sorption and desorption isotherms was less than 5% on average [46], showing a good reversibility of the measurements. In this work, we present only the sorption isotherms.

4. Results

4.1. Nafion: analysis of literature data

Experimental water uptake data for Nafion 117 can be found for example in the works of Zawodzinski et al. [50], Kreuer [51] and Alberti et al. [31].

The calculated free volume of Nafion from Equation (9) is 0.133 L mol^{-1} (see above). In this value, the primary hydration of the sulfonic acid groups situated at the interfaces of the polymer domains must be considered. Alberti showed recently by volumetric measurements at various water contents that the ionomer equivalent volume remains approximately constant for the introduction of the first four water molecules due to the electrostriction effect [25]; this value was confirmed by Benziger and co-workers [21]. If we consider a primary hydration shell with tetrahedral coordination (Eigen cation [4]) and taking into account the molar volume of H₂O, which is assumed constant, this corresponds to an increment of 0.072 L mol^{-1} . The free volume of Nafion at $\lambda = 4$ reported in Ref. [53] as 0.1 L kg^{-1} (equivalent to 0.11 L mol^{-1}) is in reasonably close agreement with the values reported above. However, recent work by Alberti et al. show that the density of Nafion can decrease to values around 1.5 kg L^{-1} after forced swelling; interlayer free volumes much larger than the ones previously considered are alluded to be the origin of this decrease [54]. In the simulation reported in Fig. 3, the volume parameter is therefore taken as an average value of 0.15 L mol^{-1} .

The elastic modulus has values in a vast range from 10 to >125 MPa, depending on the thermal treatment of the ionomer [25]. The existence of an inverse proportionality between the hydration number and the elastic modulus of Nafion was experimentally discovered by Alberti and coworkers [31]. Using the higher bond value of 125 MPa, the deformation parameter applied in the simulation of Fig. 3 is: $a = 5 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$. [53] With Equation (14), we can express the relation between the elastic modulus and the water uptake coefficient for Nafion:

$$\lambda = 30 \cdot \frac{\pi}{E} + 8 \quad (15)$$

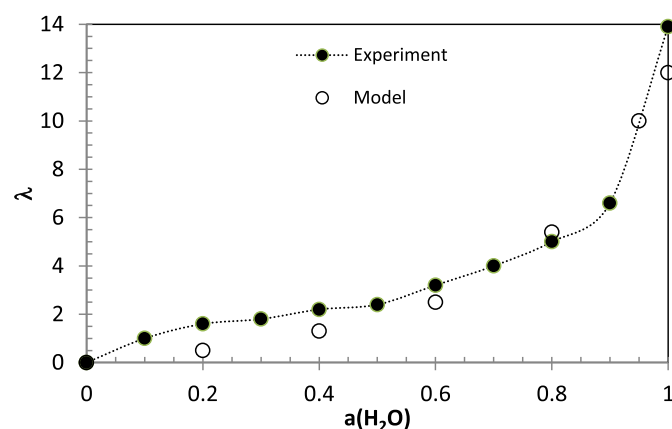


Fig. 3. Comparison of an experimental water uptake isotherm for Nafion 117 from Ref. [51] with calculated values using Equations (2), (4), (5) and (12). $\text{IEC} = 0.9 \text{ mol kg}^{-1}$, $a = 5 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$ and $b = 0.15 \text{ L mol}^{-1}$.

This expression is near the equation reported by Alberti and coworkers ($\lambda = (500/E) + 6$) [31] if the osmotic pressure is around 10 bar; indeed the mechanical measurements of Ref. [31] were made at high relative humidity (RH = 95%), where this value is realistic.

The calculated water uptake for Nafion 117 is confronted with experimental data reported by Kreuer in Fig. 3. The experimental trend is well reproduced; one should emphasize that the calculation is based on analytical equations (Equations (4), (5) and (12)) with only two constants that are calculated from measurable physical properties and without any adjustable fitting parameters. The underestimation of hydration numbers at low water activity is probably related to the fact that the first water molecules are in the primary hydration shell, where they do not contribute significantly to the osmotic pressure.

We will apply the model in the following to another important ionomer family: sulfonated aromatic polymers (SAP).

4.2. Sulfonated Poly-Ether-Ether-Ketone (SPEEK)

For sulfonated aromatic polymers, the elastic modulus is between 5 and 10 times higher than for Nafion, depending on the amount of cross-linking of the ionomer: the elastic modulus of SPEEK is in the range 600–1400 MPa [45,55]. Therefore, values of 1.5×10^{-4} or 7.5×10^{-5} L mol⁻¹ bar⁻¹ are used as deformation parameter for the modeling of experiments with uncross-linked or cross-linked (XL) SPEEK, respectively. The studied ionomers had an IEC varying in a range between 1.7 and 2.7 mol kg⁻¹ (corresponding to a Degree of Sulfonation (DS) between 0.49 and 1). The dry density of SPEEK is (1.3 ± 0.1) kg L⁻¹ (average value of 8 experiments), giving $V_{\text{dry}} = 0.28$ L mol⁻¹.

The Van der Waals volume calculated using Bondi's group contributions [38] amounts to 0.18 L mol⁻¹, whereas atomic contributions [41] lead to 0.20 L mol⁻¹ in reasonable agreement with the former value. Applying Equation (9) gives a free volume around 0.1 L mol⁻¹; a so-called “frozen-in” free volume reported in Ref. [56] for another sulfonated aromatic polymer (poly-phenylene-disulfonic acid) amounted to 0.063 L mol⁻¹. Benziger and coworkers found by volumetric experiments that 4 water molecules, corresponding to 0.072 L mol⁻¹, form the primary hydration shell in SPEEK as in Nafion [21]. The conclusion is that sulfonic acid groups in SPEEK appear associated with free volume, which permits water molecules to be sorbed with almost no change in polymer volume [21].

Fig. 4 shows experimental hydration isotherms for uncross-linked and cross-linked SPEEK together with the modeling results, obtained with a constant free volume parameter of 0.13 L mol⁻¹ [56]. The agreement with the experiment is remarkable given that all data were again obtained with only two constants and no fitting parameters; the same constants describe also very well previously published water uptake data for SPEEK [44]. We can especially observe for the cross-linked ionomer (black curve) a higher water uptake at low water activity, but a lower one at high water activity. The cross-linked membranes should therefore suffer less from dehydration at low and from swelling at high water activity, escaping the dilemma outlined in the introduction. The origin of this effect is that the ionomer with lower elastic modulus E is more sensitive to water activity and osmotic pressure changes, as can be seen in Equation (12).

4.2.1. Influence of various amounts of cross-linking

Fig. 5 shows experimental (taken from Ref. [45]) and calculated hydration isotherms for SPEEK membranes with different levels of cross-linking, obtained by thermal treatments during different times (0, 3, 10 or 24 h) at 180 °C in presence of small quantities of

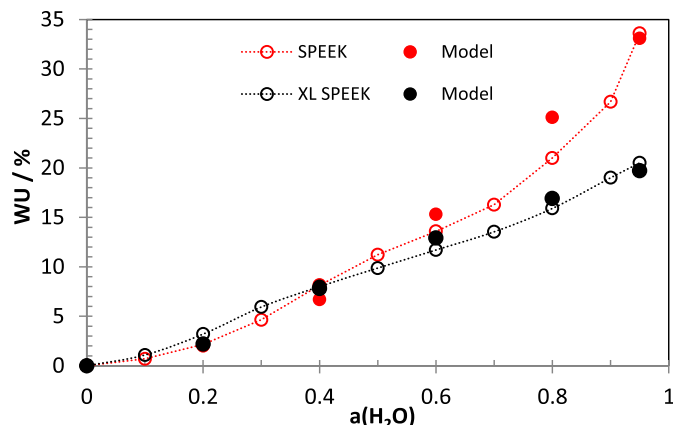


Fig. 4. Experimental water uptake isotherms for uncross-linked (IEC = 2.5 mol kg⁻¹) and cross-linked (XL, degree of cross-linking = 0.4, IEC = 1.5 mol kg⁻¹) SPEEK and results using Equations (2), (4), (5) and (12) (full symbols). The deformation parameter was taken as 1.5×10^{-4} or 7.5×10^{-5} (XL) L mol⁻¹ bar⁻¹ and the free volume parameter as 0.13 L mol⁻¹.

residual casting solvent DMSO. The measured values of IEC with different degrees of cross-linking are indicated in the left side of the legend of Fig. 5. The kinetics of the cross-linking reaction has been shown to be first order, so that the degree of cross-linking depends exponentially on the time of the heat treatment [57]. The deformation parameter was assumed to follow a similar exponential dependence (the values are reported in the right side of the legend of Fig. 5). The agreement between experiments and calculations, using only two constants determined by physical properties, is quite satisfactory. The model captures well the experimental fact that the water uptake isotherms are quite similar at low humidity, but are very different at high humidity, where cross-linking protects efficiently against excessive swelling by increasing the elastic modulus of the ionomer. One can see the inversion from higher water uptake at low humidity to lower water uptake at high humidity for more cross-linked samples.

Considering the data in Fig. 5, intermediate treatment times (between 3 and 10 h) are the most appropriate in order to avoid swelling at high humidity, but still keep a sufficient hydration at low humidity to maintain good proton conductivity [57]. The free

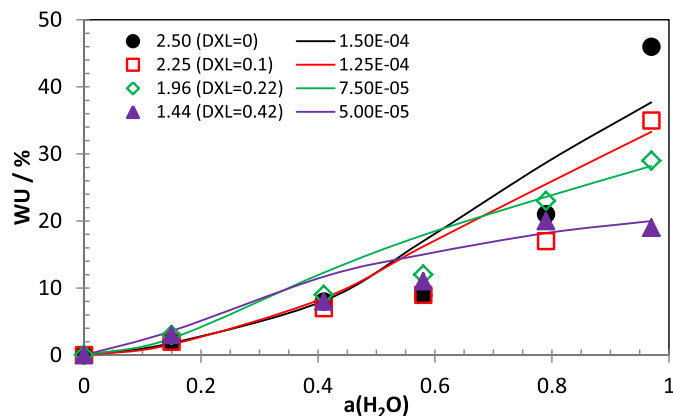


Fig. 5. Water uptake isotherms for SPEEK cast from DMSO with various degrees of cross-linking DXL (symbols: experiments, lines of the same color: model). The IEC (in mol kg⁻¹) and DXL are indicated for the different samples in the left side of the caption. The corresponding values of the deformation parameter (in L mol⁻¹ bar⁻¹) are shown on the right side of the caption; the free volume parameter was always taken as 0.13 L mol⁻¹.

volume parameter was taken as constant for all cross-linking degrees, assuming that cross-linking stabilizes the free volume of the ionomer. The good agreement with the experiments indicates that this assumption is reasonable.

4.2.2. Influence of free volume changes by annealing

Fig. 6 shows experimental and calculated hydration isotherms of SPEEK membranes cast from DMAc and annealed at different temperatures during the same time. This solvent has a relatively high boiling point and is known to interact strongly with sulfonic acid groups [58]. It has been demonstrated that the heat treatment does not induce any cross-linking [43,57] and the same deformation parameter of uncross-linked SPEEK, $1.5 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$, is consistently used for modeling all isotherms. Experimentally, the water uptake at high water activity is quite low and, paradoxically, increases with increasing the temperature of annealing. All curves can be well described by assuming initially a very low free volume (taken as 0.06 L mol^{-1}), which slightly increases by the annealing treatments (from 0.06 to 0.08 L mol^{-1}). The physical interpretation is that part of the free volume is initially occupied by remaining casting solvent DMAc, which solvates the sulfonic acid groups particularly efficiently, but is removed more and more by annealing at increasing temperature. However, the low value even at 160°C might indicate that the annealing leads globally to a reduction of free volume, as generally assumed in polymer science [59], when no cross-linking occurs.

The model reproduces the experimental fact that all isotherms are very similar at low humidity and start to differentiate only at high humidity; in other words, a larger free volume does not play any role when few water molecules are present, but is only important for larger water uptake.

4.3. Sulfonated Poly-Phenyl-Sulfone (SPPSU)

The elastic modulus of SPPSU is in the range of 500–1000 MPa for low degrees of cross-linking [46]. Therefore, the values, 2×10^{-4} or $1 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$, were used as deformation parameters for the modeling of water uptake isotherms of uncross-linked or cross-linked (XL) SPPSU, respectively. The studied ionomers had an IEC of 3.57 and 2.35 mol kg^{-1} (DS of 2 and 1.16). The dry density of SPPSU

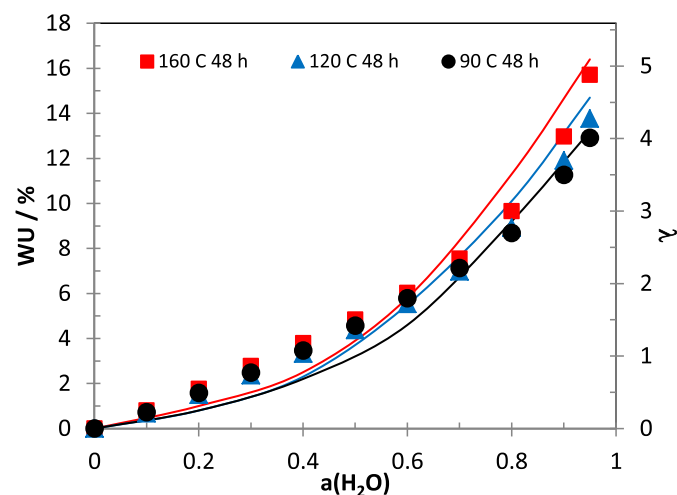


Fig. 6. Experimental water uptake isotherms for SPEEK cast from DMAc and annealed at various temperatures for 48 h. Experimental results are shown as full symbols; calculated isotherms using Equations (2), (4), (5) and (12) as lines with the same color. The deformation parameter is consistently taken as $1.5 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$ and the free volume parameter as 0.06 (90°C), 0.07 (120°C) or 0.08 (160°C) L mol^{-1} .

was measured as $(1.5 \pm 0.4) \text{ kg L}^{-1}$; its dry volume is 0.38 L mol^{-1} . The Van der Waals volume calculated using group contributions [38] (0.27 L mol^{-1}) or atomic contributions [41] (0.28 L mol^{-1}) are quite similar and give a smaller free volume than in the previous cases. For that reason, the model data were obtained with a free volume parameter of 0.1 L mol^{-1} , assumed unchanged by the heat treatment as in the case of SPEEK.

Fig. 7 shows the water uptake isotherms of un-cross-linked and cross-linked SPPSU. Experimental results and calculated isotherms are in good agreement. The water uptake of XL-SPPSU is significantly lower only at high water activity. The lower value of the free volume in comparison to SPEEK can be attributed either to a larger quantity of casting solvent remaining in the ionomer, due to the larger density of sulfonic acid groups, or to the straighter and more rigid macromolecular chains of PPSU.

5. Discussion

5.1. Influence of deformation and free volume parameters

Fig. 8 shows calculated hydration isotherms for different values of the deformation parameter with a free volume always taken as 0.15 L mol^{-1} and $\text{IEC} = 2.7 \text{ mol kg}^{-1}$. One can observe the effect of a change of the elastic modulus, for example by cross-linking the polymer or removing a plasticizing solvent, on the hydration. The highest value of a , corresponding to a soft ionomer, gives a strong change of water uptake with water activity that can actually be well described by an exponential equation (black curve in the figure). Lower values of a , corresponding to stiffer ionomers, give sigmoidal water uptake curves (blue curve with triangles in the figure) that are observed in many experiments. The point of inflection shifts to lower water activity for a lower deformation parameter.

One can also notice that the water uptake at low water activity is actually higher for stiff ionomers with a low deformation parameter. There is thus an intersection between hydration curves of “softer” and “stiffer” ionomers at a certain water activity (see Fig. 8). This behavior might seem paradoxical at the first glance, but it is observed experimentally. The physical origin is the fact that an ionomer with high deformation parameter is more reactive to changes of osmotic pressure; it has thus a larger water uptake at high water activity, and a lower one at low water activity.

The influence of the second parameter, “free volume”, is shown in Fig. 9 for a constant deformation parameter, taken as

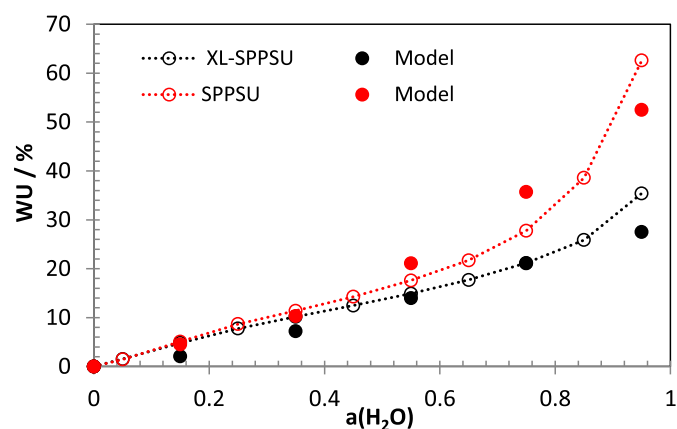


Fig. 7. Experimental water uptake isotherms for uncross-linked ($\text{IEC} = 3.57 \text{ mol kg}^{-1}$) and cross-linked (XL, degree of cross-linking = 0.34, $\text{IEC} = 2.35 \text{ mol kg}^{-1}$) SPPSU and results using the Equations (2), (4), (5) and (12) (full symbols). The deformation parameter was taken as 2×10^{-4} or $1 \times 10^{-4} \text{ L mol}^{-1} \text{ bar}^{-1}$ (XL) and the free volume parameter in both cases as 0.1 L mol^{-1} .

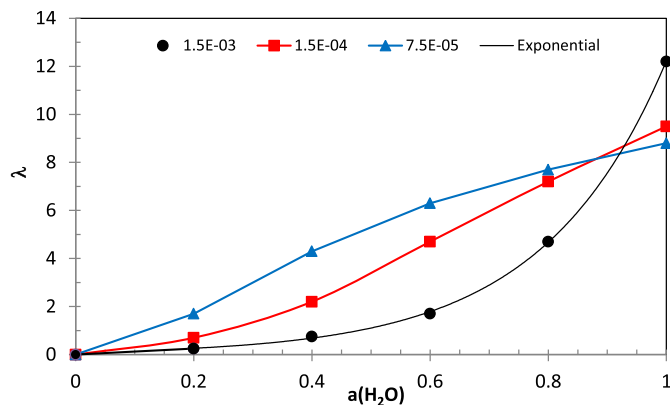


Fig. 8. Hydration isotherms for different values of the deformation parameter (indicated in the figure in $\text{L mol}^{-1}\text{bar}^{-1}$) with a constant free volume parameter $V_{\text{free}} = 0.15 \text{ L mol}^{-1}$ and $\text{IEC} = 2.7 \text{ mol kg}^{-1}$.

$1.5 \times 10^{-4} \text{ L mol}^{-1}\text{bar}^{-1}$. One can observe a significant increase of the water uptake at the highest water activity, when the free volume changes from low to high values, from “closed” to “open” ionomer structures. However, even for large free volume parameters the hydration never increases exponentially, unlike for large deformation parameters (see Fig. 8). At low water activity, e.g. $a(\text{H}_2\text{O}) = 0.2$, the hydration is very similar whatever the free volume, because the open space inside the matrix is not used, as the number of water molecules is small.

5.2. Critical assessment and predictions of the model

We have already discussed the fact that the interface and electrostatic energy terms in the Gibbs free energy variation are not considered in our model, because there is no simple analytical expression for these terms, which depend also on the particular shape assumed for the hydrated domains that is very complicated and not well known. Nevertheless, our simplified model describes the experiments globally well, but its other assumptions should be critically assessed. The most critical point concerns the assumed linear relation between the volume of the electrolyte solution inside the ionomer and the osmotic pressure. By assuming linearity, we suppose that the ionomer shows elastic behavior. Furthermore, we use one unique set of constants (deformation parameter and free volume parameter) for the entire range of water activity studied ($0 < a(\text{H}_2\text{O}) < 0.95$). The good agreement with the

experiments shows that there is indeed no need to consider irreversible plastic behavior in the range of humidity considered here. At the largest humidity levels ($a(\text{H}_2\text{O}) > 0.95$) and especially in liquid water, pure elastic behavior can however not always be assumed. This is probably related to the Schröder paradox [50], which has been associated to the Laplace pressure of hydrated domains [32].

The second critical point is the assumption of an ideal system from the point of view of thermodynamics. Obviously, we are studying quite concentrated electrolytic solution and these concentrations are much higher than the limits for the application of an ideal formalism, using molar fractions and molar volumes instead of activities and partial volumes, or even of Debye–Hückel limiting laws [37]. Some comprehensive results on colligative properties in Nafion have been presented [25], but there are not enough data available to deduce activities or partial molar volumes in other hydrated ionomers, although a very small negative volume of mixing, $\Delta V_{\text{mix}}/\lambda < -10^{-4} \text{ L mol}^{-1}$, was recently reported for SPEEK [22]. A further improvement of the agreement between the numerical and experimental results by fitting concentration-dependent variables, although quite possible, would bring nothing from the point of view of physical understanding.

Given the satisfying agreement with experiments, the advantage of our simple model is that we can use it to predict water uptake properties of ionomers and ways to improve them.

The free volume in a polymer can be reduced in principle either by annealing treatments at moderate temperature or by filling it with another component, such as a solvent with high boiling point and strong interactions with the polymer matrix. This can participate in an efficient reduction of the water uptake at low temperature, as shown experimentally with dimethylacetamide, a basic solvent that strongly interacts with sulfonic acid groups. However, this strategy is less efficient at high temperature as the solvent gets finally removed and the liberated free volume can then get flooded with water. In order to optimize such a solvent effect, the solvent should have the highest possible molar volume (to fill most of the unoccupied space), have a low solubility in water, a high boiling point and strong interactions with the ionomer (to stay inside the ionomer even during long times and at higher temperature) and have the lowest possible dielectric constant, in order to maintain the interactions between macromolecular chains and keep the elastic modulus of the ionomer as high as possible (and, hence, avoid swelling by an increase of the deformation parameter). It might be difficult to find a solvent reconciling all these requirements in practice.

Therefore, the formation of cross-linking bonds throughout the ionomer matrix, enhancing the elastic modulus of the ionomer and reducing its deformation parameter, appears as a better option. The lower deformation parameter limits not only swelling at high water activity, but also dehydration at low humidity. It can thus be considered an excellent way to improve the hydration properties over the whole humidity range [60]. The limited changes in hydration should also improve the durability and lifetime of cross-linked ionomers under fuel cell operation conditions, like on–off cycles in electric vehicles.

6. Conclusions

A simplified physical model was developed to describe and predict the hydration isotherms of acidic ionomers. The model is based on a linear relation between the volume of the electrolytic solution inside the ionomer and the osmotic pressure exerted by the water. It helps to understand hydration, where more sophisticated models require significant computational efforts.

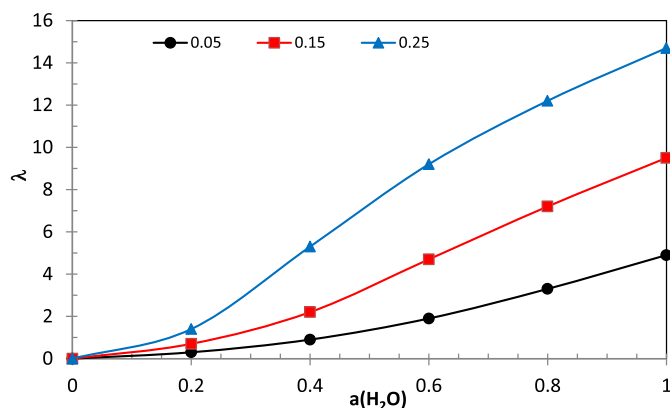


Fig. 9. Hydration isotherms for different values of the free volume parameter (indicated in the figure in $\text{L mol}^{-1}\text{bar}^{-1}$) with constant deformation parameter $1.5 \times 10^{-4} \text{ L mol}^{-1}\text{bar}^{-1}$ and $\text{IEC} = 2.7 \text{ mol kg}^{-1}$.

Experimental water uptake isotherms for Nafion, SPEEK and SPSPSU ionomers are well described as function of only two physically meaningful constants – the deformation parameter, which is inversely proportional to the elastic modulus of the ionomer, and the free volume parameter – and without any adjustable fitting parameters. The model is consistent with an elastic behavior of the studied ionomer in the investigated range of water activity ($0 < a(\text{H}_2\text{O}) < 0.95$).

Different strategies to optimize the hydration properties of ionomers were discussed. An important prediction of the model, verified by the experiments, is that hydration variations between low and high water activity, which are very harmful for the durability of ionomers in fuel cells, can be most efficiently limited by a suitable degree of cross-linking of the ionomer matrix.

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